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### Effect of mechanical grinding on physical and chemical characteristics of circulating fluidized bed fly ash from coal gangue power plant



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#### HIGHLIGHTS

• We examine the characteristics differences between CFB-FA and OFA.

• The effects of mechanical grinding on the CFB-FA characteristics were investigated.

• The grinding efficiency of CFB-FA can be improved by organic grinding aids.

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#### ABSTRACT

To characterize roles of mechanical grinding on the physical and chemical characteristics of circulating fluidized bed fly ash (CFB-FA), the differences between CFB-FA and ordinary fly ash (OFA) were revealed and the effects of mechanical grinding action on the physical and chemical characteristics of CFB-FA were studied from grinding kinetics, particle size distribution, bulk density, morphology, pore size distribution, amorphous substance content, anionic polymerization degree and hydration property and so on. The results indicate that there are some differences in chemical and mineral composition, particle morphology and self-hardening property between untreated CFB-FA and OFA. The particle size distribution of CFB-FA is optimized by mechanical grinding and the optimization role is best at 50 min grinding time. Mechanical grinding action can also reduce the interconnected pores, average pore radius, total cumulative pore volume and the pores content in range of greater than 3 nm radius of CFB-FA. Meanwhile, the amorphous substance dissolution amount of CFB-FA is increased and the polymerization degrees of [SiO<sub>4</sub>] and [AlO<sub>6</sub>] are reduced by mechanical grinding. All the 3d, 7d and 28d strengths of ground CFB-FA paste are improved significantly, and 3d and 28d activity index of the CFB-FA are also improved by more than 5% and 14%, respectively. Furthermore, organic grinding aids can further improve the mechanical grinding roles on CFB-FA and the role of ethylene glycol is the most excellent.

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#### 1. Introduction

Circulating fluidized bed (CFB) combustion technology is an efficient, low pollution, clean coal-fired technology, which is being developed rapidly in the past two decades. It has many advantages that other combustion modes can't match [1-4]: (1) it has a high combustion efficiency; (2) due to its low temperature combustion mode, the emissions of NO<sub>X</sub> is far lower than that of the ordinary pulverized coal boiler and the desulfurization can be done directly in the combustion process; (3) it also has a wide adaptability for fuel, i.e., all the ordinary bituminous coal, anthracite, lignite, peat, coal gangue, etc. can be used as fuel of CFB combustion [3,5,6].

http://dx.doi.org/10.1016/j.conbuildmat.2015.10.144 0950-0618/© 2015 Elsevier Ltd. All rights reserved. Based on these advantages, CFB combustion technology has been popularized and applied in China in recent years. Coal gangue is the maximum emissions of solid waste from coal mine production and is also one of the largest generation and accumulation amount of industrial solid wastes in China. In recent years, coal gangue is used as CFB boiler fuel to generate electricity and supply heat in China, which provide an effective utilization way for coal gangue [7–9].

With the extension and large-scale development of CFB coalfired technology in China, the emissions of CFB fly ash (CFB-FA) are increasing rapidly and the amount of CFB-FA will become larger and larger. Currently, more than 50 million tons of CFB fly ash and slag are discharged annually in China. However, for a long time, almost all the CFB-FA are not utilized and discharged directly into storage sites, which not only waste resources, but also occupy

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land and pollute environment [5,10–13]. Thus, the effective resources utilization of CFB-FA is desperately needed. As the combustion temperature of CFB boiler (850–900 °C) is much lower than that of ordinary pulverized coal fired boiler (up to 1500 °C), resulting in that there are fundamental differences in the formation mechanism between CFB-FA and ordinary pulverized coal fired boiler fly ash (OFA). Thus, it results in the big differences in the physical and chemical characteristics between CFB-FA and OFA [14,15]. The existing research literatures have demonstrated that CFB-FA also has the pozzolanic activity similar to OFA, even has a selfhardening property [16,17], thus it shows that CFB-FA has great potential as the supplementary cementitious materials used in cement and concrete field. Meanwhile, it also provides a good way for the effective utilization of CFB-FA. However, many studies [18–20] have shown that the physical and chemical characteristics of untreated fly ash are generally poor (for example, the particles are coarse and uneven: their surfaces are adherent and polyporous: chemical active is low), which results in a poor application performance for CFB-FA as supplementary cementitious materials used in cement and concrete. The physical and chemical characteristics of fly ash usually can be improved by mechanical grinding action, which make it get an excellent application performance [21,22].

In this paper, the CFB-FA from coal gangue plant was selected as the research object. The differences of physical and chemical characteristics between CFB-FA and OFA were analyzed from some aspects such as particle size and its distribution, chemical and mineral composition, particle morphology and self-hardening. On this basis, the effects of mechanical grinding action on the physical and chemical characteristics of CFB-FA were studied from grinding kinetics, particle size distribution, bulk density, morphology, pore size distribution, amorphous substance content, anionic polymerization degree and hydration characteristics. The roles of organic grinding aids on CFB-FA were also discussed.

#### 2. Experimental

#### 2.1. Materials

The untreated CFB-FA and OFA were supplied from Pingshuo Coal Gangue Power Plant and Shentou Power Plant of Shanxi province, respectively. The sieve residue of OFA selected was close to that of CFB-FA.

The organic grinding aids used included triethanolamine (TEA), ethylene glycol (EG), glycerol (GLY) and modified triethanolamine (i.e., triethanolamine acetate) (M-TEA), all the grinding aids were chemical reagents except that M-TEA was self-made in laboratory.

#### 2.2. Grinding experiment

Grinding experiment of CFB-FA was carried out by using laboratory ball mill. The type of ball mill is  $\Phi$ 500 mm  $\times$  500 mm, 48 r/min and closed circuit, and the grinding media is composed by 60 kg steel balls ( $\Phi$ 40 mm,  $\Phi$ 50 mm,  $\Phi$ 60 mm and  $\Phi$ 70 mm) and 40 kg small steel forgings ( $\Phi$ 25 mm \* 35 mm). The weight of CFB-FA for each grinding was 5 kg and the grinding time was 10 min, 15 min, 20 min, 25 min, 30 min, 35 min, 40 min, 45 min, 50 min and 60 min, respectively. In addition, the grinding time of CFB-FA was 20 min in the grinding aids experiment, the control group (blank group) was not added into grinding aids and the experiment group was added into 0.05 wt% grinding aids.

#### 2.3. Test methods

- (1) The chemical composition of CFB-FA was measured by X-ray fluorescence (XRF) according to the Chinese National Standard GB/T176-2008. The mineral composition was analyzed by X-ray diffraction (XRD). The XRD measurement was conducted with a D6000 diffractometer using nickelfiltered Cu Kal radiation (=1.5405 Å, 40 kV and 40 mA) from Shimadzu company of Japan.
- (2) The sieve residue and specific surface area of CFB-FA were measured according to the Chinese National Standard GB/T1345-2005 and GB/ T8074-2008, respectively. The particle size distribution was measured according to the Chinese Industry Standard JC/T721-2006.
- (3) The loose bulk density of CFB-FA was measured by the following method: CFB-FA was injected into a certain weight (denoted by W<sub>0</sub>) and volume

(denoted by *V*) of container, and the total weight (denoted by *W*) of the container and the powder was weighed after filling up the container, then the loose bulk density (denoted by  $\rho$ ) of CFB-FA was measured by according to the formula: [ $\rho = (W - W_0)/V$ ].

- (4) The particle morphology of CFB-FA was observed by Hitachi S-3400 scanning electron microscope (SEM).
- (5) The pore size distribution of CFB-FA was measured by BET static adsorption apparatus according to the Chinese National Standard GB/T19587-2004.
- (6) The dissolved amount of amorphous substance of CFB-FA was determined by hydrofluoric (HF) acid dissolution method [23], as follows: Firstly, 4% concentration (volume fraction) HF acid solution was prepared and takes 100 ml HF acid solution placed into a plastic beaker; Then, took 2 g (accurate to 0.001 g) CFB-FA added into HF acid solution and the mixture was stirred sufficiently; Where, the environmental conditions was 60 °C water bath and stirring was continued for 3 h; And then, the solution in beaker was filtered and the filter residue was dried to constant weight and weighed. Thus, dissolved amount of amorphous substance of CFB-FA could be determined by calculating the weight loss of dissolving before and after for CFB-FA in HF acid.
- (7) The anionic polymerization degree of CFB-FA was analyzed by Nicolet iS 10 Fourier transform infrared spectroscopy (IR).
- (8) The self-hardening property of untreated CFB-FA was tested as follows: Firstly, CFB-FA was mixed with water to produce paste. The water-binder ratios of paste are 0.4 and 0.5, respectively. Then test specimens were prepared in cuboid molds of length 160 mm, width 40 mm and height 40 mm. The test specimens were cured at 20 ± 1 °C and >95% humidity for 7d and 28d, respectively. The picture of self-hardened species is shown in Fig. 1. Then the strength of test blocks was measured according to the Chinese National Standard GB/T17671-1999.
- (9) The hydration property of ground CFB-FA was tested as follows: The CFB-FA paste was firstly prepared from 75 wt% CFB-FA, 25 wt% CaO and water by stirring uniformly, and the water-binder ratio of paste was 0.5. And the specimens were cured at  $20 \pm 1$  °C and >95% humidity for 3d, 7d and 28d, respectively. Then the strength of CFB-FA could be measured according to the Chinese National Standard CB/T17671-1999.
- (10) The activity index of CFB-FA was measured according to the Chinese National Standard GB/T12957-2005. The mortar test specimens were prepared by using the proportions for the mortar mix given in Table 1. Then the specimens were cured at  $20 \pm 1$  °C and >95% humidity. The compressive strengths of the mortar were determined at 3d and 28d, respectively. So the activity index of CFB-FA was determined from:

$$A_3 = (R_3/R_{03}) \times 100, \quad A_{28} = (R_{28}/R_{028}) \times 100$$

where,  $A_3$ ,  $A_{28}$  were the 3d and 28d activity index of CFB-FA, respectively, (%);  $R_3$ ,  $R_{28}$  were the 3d and 28d strength of blender mortar, respectively, (MPa); and  $R_{03}$ ,  $R_{028}$  were the 3d and 28d strength of pure cement mortar, respectively, (MPa).



Fig. 1. Self-hardened specimens.

Table 1

Mortar mixture proportions used for activity index test of CFB-FA.

	Cement (g)	CFB-FA (g)	China ISO standard sand (g)	Water (g)	W/ B
$R_0$	450	-	1350	225	0.5
R	315	135	1350	225	0.5

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